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THE EFFECT UPON PERMEABILITY OF (I) THE SAME SUBSTANCE AS CATION AND ANION, AND (II) CHANGING THE VALENCY OF THE SAME ION

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I. The Effect of the Same Substance as Cation and Anion

In a recent paper (1) facts were presented which indicate that polyvalent cations do not cause an increase in the resistance of Laminaria if they are combined with polyvalent anions, and it seems natural to suppose that the difference between the action of a salt with a bivalent cation and a monovalent anion, *e.g.*, $MgCl_2$, and one with a bivalent cation and a bivalent anion, such as $MgSO_4$, is due to the extra charge on the anion. Cations seem to cause an increase in resistance and anions a decrease. In $MgCl_2$ the action of the cation is dominant; in $MgSO_4$, the action of the anion.

If this effect is due to electrical charge, we may ask what will happen if the same ion is used as cation and as anion. This problem seems at first glance to present great difficulties because it is necessary to work with solutions which are not strongly acid or alkaline. Certain elements (such as aluminum, arsenic, chromium, etc.) exist both as cations and as anions, but they are very weak acids or bases and solutions of their salts are not neutral.

The difficulty may be surmounted in a measure, however, by adding enough acid to the alkaline solution to bring its pH value down to that of the acid solution. If necessary the conductivity may be increased by mixing with a neutral salt (*e.g.*, NaCl).

For this purpose, chromous chloride, sodium chromate, chromic acid, and sodium chloride were used. The chromous chloride is not soluble enough to make the conductivity equivalent to that of normal sea water, and in order that the osmotic pressure of the sea water (with which the solution is compared) should not be too low, the chromous chloride was mixed with sodium chloride. The final solution was then composed of 50 percent chromous chloride 0.61 M and 50 percent sodium chloride 0.52 M. This mixture has greater electrical resistance than sea water and has a pH of about 4.5 as determined by the hydrogen electrode.

When tissue is transferred to this mixture from diluted sea water of the same conductivity, the following changes in resistance are observed (see fig. 1, *A*):

Time in Minutes	Percentage of Original Resistance	Probable Error of the Mean Expressed as Percentage of the Mean (Three Experiments)
2	101	0%
5	102	1
10	92	1
20	75	6
40	51	8
60	47	11
80	46	11

It is seen that there is a slight rise of resistance which is quickly followed by a fall. That the rise is no greater may be due to the facts that (1) the chromium ion used carries only two charges, and (2) the dilution with the sodium chloride would also tend to cause an immediate fall in resistance.

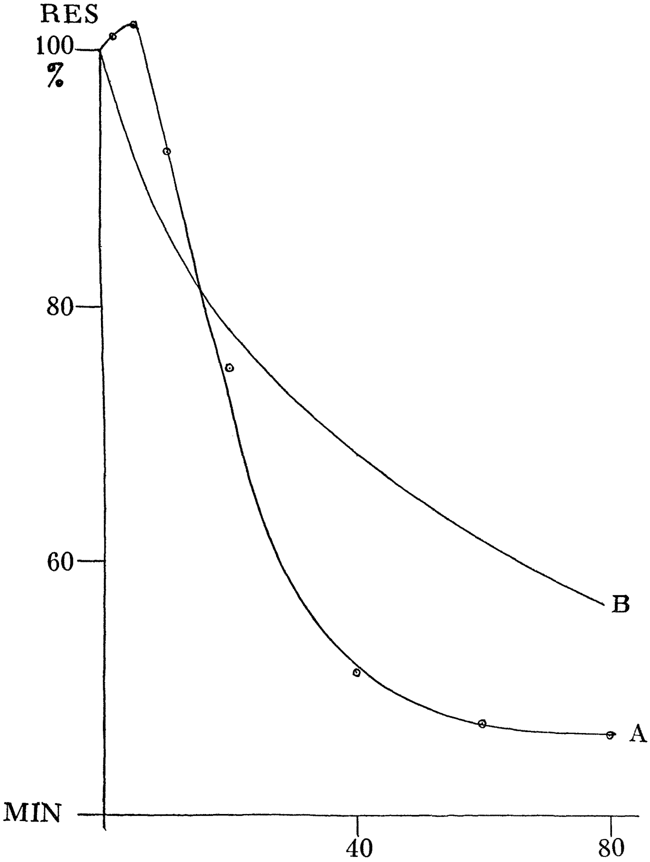

FIG. 1. *A*. Effect of 50 percent $CrCl_2$ 0.61 M plus about 50 percent NaCl 0.52 M upon the permeability of *Laminaria Agardhii* Kjellm. Ordinates indicate percentage of the original resistance (considered as 100 percent) in sea water of the same conductivity as the solution tested. Abscissae represent time in minutes of the tissue in the solution. *B*. Effect of a solution of 50 percent Na_2CrO_4 0.22 M and 50 percent NaCl 0.52 M with enough chromic acid added to produce the same pH as in *A* (pH 4.5).

Sodium chromate of 0.22 M has about the same conductivity as normal sea water and has a pH of about 9.5. This is not alkaline enough to cause any appreciable effect, just as a pH of 4.5 was not acid enough to interfere with the success of these experiments, as shown by Osterhout (2). Nevertheless, in order that conditions might be comparable with those in which chromium was used as a cation, a solution was prepared consisting of 50 percent sodium chromate 0.22 M, 50 percent sodium chloride 0.52 M, and with just enough chromic acid added to bring the acidity up to that of the chromous chloride solution (pH about 4.5).

The acidity in the case of colored solutions was measured by diluting a hundred times, taking the pH of this diluted solution, and then making a correction for the increase in dissociation upon dilution. As a check upon this method the pH was also determined directly by means of the hydrogen electrode.

The results obtained with the sodium chromate mixture of pH 4.5 are shown below and in figure 1, *B*. The figures given are the average of three experiments.

Time in Minutes	Percentage of Original Resistance	Probable Error
2	93	1%
5	88	1
10	85	2
20	78	2
40	68	3
60	62	3
80	55	5

It is seen that the initial effect is a fall in resistance. This is to be expected since we have here a monovalent cation with a bivalent anion. It is also seen that the hydrogen-ion concentration is not responsible for the rise in resistance when the chromium has a positive charge. When it has a negative charge (even though the hydrogen-ion concentration is the same, *viz.*, pH 4.5) the resistance does not increase but, on the contrary, decreases from the start. To what extent this is due to the presence of the oxygen in the anion can not be determined.

II. The Effect of Changing the Valency of the Same Ion

As previously stated, the nature of the charge on the ion seems to be a very important factor in determining the initial response of the tissue to electrolytes. It is natural to inquire what the result would be if the same ion could be used with a varying charge. If an anion with one charge causes a decrease in resistance, the same ion with two or three charges should cause a more rapid decrease. Similarly, a cation with two positive charges should cause a less rise in resistance than one with three provided they are used with anions which permit this rise in resistance. Osterhout found in general a greater increase in resistance with trivalent and tetravalent cations (3) than with bivalent cations (4), but he did not compare the effects of the same ion with different charges.

The choice of ions for this purpose is very limited. Antimony, arsenic, and tin can not be used because of their weak basicity which results in extremely acid solutions. The toxic action of copper is a sufficient reason for not using it. The insolubility of mercurous, chromic, and cobaltic salts almost prohibits their use. This leaves iron as a possibility among the common cations of variable valency.

For this study $FeCl_3$ and $FeCl_2$ were used. The solution of $FeCl_3$ was 0.20 M and had a pH value of about 2.5. When the tissue was placed in such a solution having the same conductivity as normal sea water, there occurred a very sudden and temporary rise in resistance followed by a rapid fall. The following table and figure 2, *A* show the results:

Time in Minutes	Percentage of Original Resistance	Probable Error (Three Experiments)
2	125	1%
5	107	1
10	71	5
20	55	9
40	47	8
60	44	7
80	42	7

The tissue becomes extremely hard and decidedly yellow in color, which seems to be due to the acid reaction of the solution. Inasmuch as the acidity of the ferric chloride lies outside the ineffective limit (2), a certain amount of the rise in resistance shown above is doubtless due to the hydrogen ions present.

The $FeCl_2$ solution of the same conductivity as that of $FeCl_3$ used is about 0.28 M and has a pH of about 4, but in order to compare the effect of the valency the solution was acidified by the addition of HCl. The acidity of these solutions (since colored ions are present) is measured and compared in the same way as that of the solutions discussed in the previous section. The final solution used consisted of 45 g. $FeCl_2$ per liter with enough HCl added to make a solution of the same conductivity and the same pH as the solution of $FeCl_3$. The results of this set of three experiments are given below and in figure 2, *B*.

Time in Minutes	Percentage of Original Resistance	Probable Error
2	118	4%
5	91	5
10	68	5
20	46	4
40	31	6
60	28	3
80	27	3

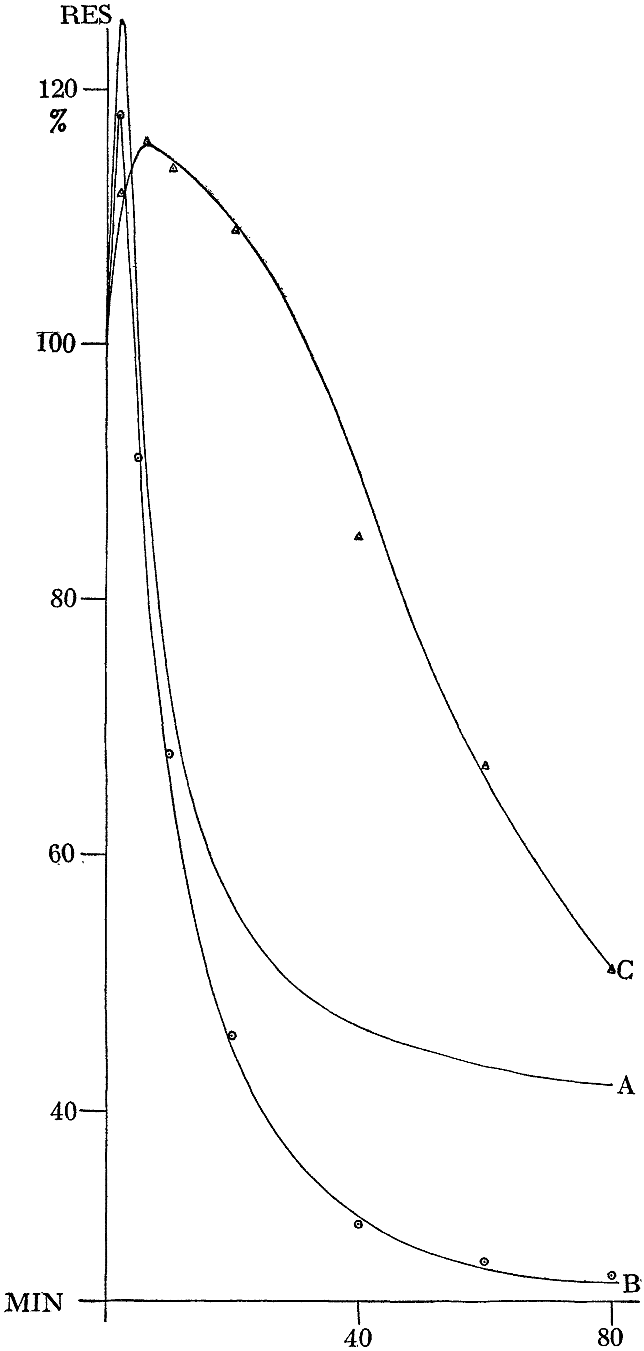

FIG. 2. *A*. Effect of $FeCl_3$ 0.20 M upon the permeability of *Laminaria Agardhii* Kjellm. Ordinates indicate percentage of the original resistance (considered as 100 percent) in sea water of the same conductivity as the solution tested. Abscissae represent time in minutes of the tissue in the solution. *B*. Effect of $FeCl_2$ 0.23 M with enough HCl added to produce the same hydrogen-ion concentration as in *A* (pH 2.5). *C*. Effect of $FeCl_2$ 0.28 M of the same conductivity as *A* and *B* (pH 4).

It is to be noted that the two curves are similar. The ferrous curve lies a little below the ferric curve. Even though the two are of the same acidity, the ferric causes a greater rise in resistance at the start than the ferrous solution. The additional positive charge on the cation seems to be the chief cause of the difference between these two solutions.

In order to see how much of the action of these salts is due to the high acidity, a third set of experiments was performed using 0.28 M $FeCl_2$ of the original pH (about 4). This concentration is the equivalent of a 0.0001 N HCl solution and, as mentioned above (2), this degree of acidity has been found to have no appreciable effect upon the permeability of Laminaria. The results of these three experiments are shown below and in figure 2, *C*.

Time in Minutes	Percentage of Original Resistance	Probable Error of the Mean
2	112	1%
5	116	2
10	114	4
20	109	3
40	85	4
60	67	7
80	51	10
100	40	10

The tissue here retains its original color and (as shown by the table and figure) the increase in resistance takes more than twice as long to reach a maximum. The general behavior and appearance of the tissue is very different from that in the two previous cases, and has in common with them only the initial increase followed by a decrease in resistance. The greater rise in the ferric chloride is not due to the concentration, since the ferric chloride is really less concentrated than the ferrous, the former being 0.20 M and the latter 0.23 M.

The conclusion would seem to be that in the case of curves *A* and *B* the primary factors are the ferric, ferrous, and chlorine ions while the hydrogen ion plays a subordinate role. The acidity causes the maximum rise to be arrived at much earlier and causes the extremely rapid fall. The valency of the cation, however, determines largely the height to which the resistance rises.

SUMMARY

1. Chromium has a different initial effect upon the permeability of Laminaria depending upon whether it occurs in the cation or in the anion of a salt. If it is in the anion, the first effect is a decrease in resistance, and if in the cation, an increase.

2. Ferric chloride causes a greater increase in resistance than ferrous

chloride, independent of the hydrogen-ion concentration. The difference seems to depend upon the valency.

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